

Effect of zirconia additions on the reaction sintering of aluminium titanate

H. A. J. THOMAS, R. STEVENS, E. GILBART
School of Materials, University of Leeds, Leeds LS2 9JT, UK

Yttria-stabilized zirconia was added to a chemically prepared mixture of alumina and titania. The effect of the zirconia on the microstructure and resultant properties was studied following reaction sintering to form aluminium titanate. An increase in mechanical strength was observed with little effect on the excellent thermal properties of the aluminium titanate. This was attributed to generation of extra microcracks by the transformation of the zirconia phase and the unusual microstructure produced by the presence of zirconia.

1. Introduction

Aluminium titanate is a material showing considerable promise in its use in a number of applications, particularly as a thermal insulator in exhaust parts and as a refractory. Full exploitation of its commercial value is hindered by two major inherent drawbacks. Firstly, the very low mechanical strength, caused by thermal expansion anisotropy-induced microcracking, and secondly, by the tendency to decompose to alumina and titania between the temperatures of 750 and 1300 °C [1]. Both of these problems have been successfully alleviated or removed using small amounts of secondary additions [2, 3]. However, it is the presence of microcracks that gives aluminium titanate its excellent thermal properties [4]. It would, therefore, be of considerable benefit to the more extensive use of the material if the mechanical strength and the stability could be improved without degrading the thermal properties.

The purpose of this study was to examine the effects of adding zirconia, stabilized with 3 mol % yttria, on the properties of an aluminium titanate prepared from an ultrafine mixture of alumina and titania. This work formed part of a more comprehensive study on the reaction sintering of aluminium titanate [5].

2. Experimental procedure

An ultrafine mixture of alumina and titania was prepared by coprecipitating the combined isopropoxides (Titanium Intermediates Ltd, Alfa Products Ltd) into a water/alcohol solution. Calcination of the dried coprecipitate at 950 °C resulted in an equimolar mixture of α -alumina and rutile, determined quantitatively by X-ray diffraction. A more detailed explanation of the procedure involved can be found elsewhere [5].

A submicrometre zirconia powder, stabilized with 3 mol % yttria (Toyo Soda Ltd), was added to the calcined alumina/titania powder by a simple wet ball milling technique, using alumina grinding media, for a milling time of 18 h. Three levels of addition were chosen of 3, 5 and 8 wt %.

Following drying and sieving, the powder was wet-bag isopressed at 200 MPa. The green bars were machined to rods on a lathe and cut into pellets 6 mm high and 9 mm diameter for the sintering experiments.

Sintering characteristics were studied with the aid of dilatometry experiments using equipment designed and constructed in the Division of Ceramics, Leeds University. Computer control allowed for continuous data acquisition with changing temperature, throughout the experiments. The data was presented in the form of shrinkage or shrinkage rate, related to the thickness of the green sample, as a function of sintering temperature. Heating rates were set at 5 °C min⁻¹ for sintering experiments. The same equipment was also used to collect thermal expansion data using a heating rate of 2 °C min⁻¹.

The extent of reaction and the identification of phases was accomplished using X-ray diffraction. Microstructural analysis was performed using standard SEM and TEM techniques.

3. Results and discussion

Fig. 1 demonstrates the effect of firing temperature on the relative density for the three levels of zirconia addition. At the temperatures employed, the reaction to form aluminium titanate was complete and the only phases present were aluminium titanate and zirconia. The zirconia existed as a mixture of the tetragonal and monoclinic phases, as identified by X-ray diffraction (XRD). The relative ratios of the two phases were dependent on the firing temperature, as shown by Fig. 2. From Fig. 1 it is apparent that the relative density increased with the firing temperature and the level of zirconia. This is the opposite of the effect observed for pure aluminium titanate in which an increase in microcrack formation with sintering temperature causes a corresponding reduction in the relative density. The improved density of the zirconia-doped samples was reflected in an increase in the mechanical integrity of the sintered samples.

Sintering dilatometry confirmed these observations,

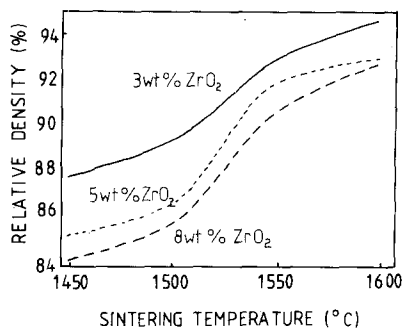


Figure 1 Relative density as a function of temperature for zirconia-doped samples of aluminium titanate.

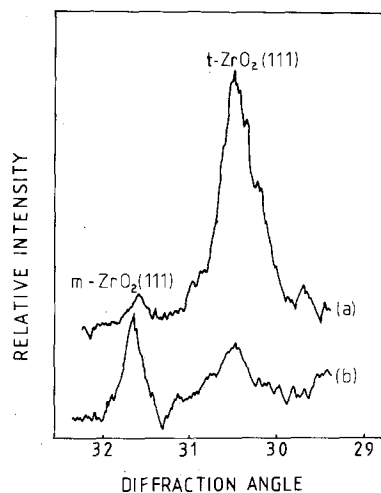


Figure 2 XRD traces of samples of ZrO_2 sintered at (a) 1360°C, (b) 1600°C.

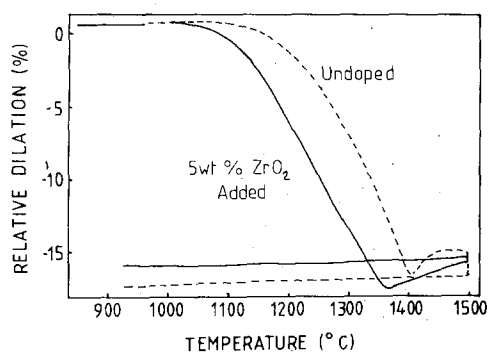
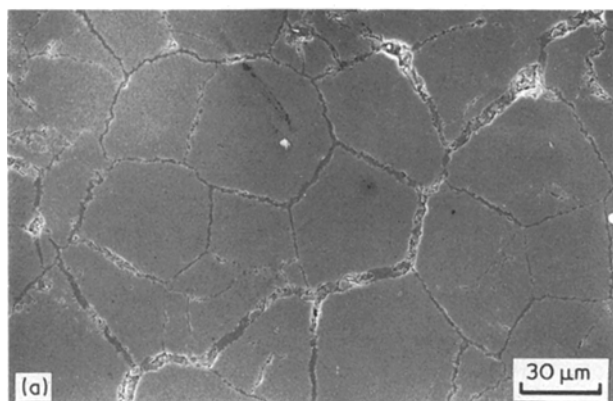


Figure 3 The effect of a zirconia addition on the relative dilation.



as shown in Fig. 3. This figure compares the dilatometry curves obtained for pure aluminium titanate and that containing 5 wt % zirconia, sintered to 1500 °C at 5 °C min⁻¹. It demonstrates that the material containing zirconia generated a greater degree of shrinkage on completion of the experiment. The form of the two curves is similar although the initiation of shrinkage is suppressed by the zirconia. This also means the reaction to form aluminium titanate, characterized by the minimum in the curve followed by expansion, is displaced to higher temperatures. However, with the zirconia addition the expansion generated by the reaction to form aluminium titanate (caused by the lower density of aluminium titanate) is fully recovered by subsequent shrinkage with increased temperature, whereas the pure aluminium titanate continues to expand.

Fig. 4 compares the polished surface microstructures obtained for pure and zirconia-doped aluminium titanate observed in the SEM. It is clear from the obvious differences in these microstructures that the zirconia, which can be seen as the white phase in Fig. 4b, had a marked effect on the nucleation and growth of the aluminium titanate grains. The result of the incorporation of zirconia is the development of an inhomogeneous microstructure of elongated grains of various sizes. The zirconia appeared to be distributed along the grain boundaries although some particles can be seen within the aluminium titanate grains. These are better illustrated by Fig. 5 and it is believed that they had become entrapped during the rapid growth of the aluminium titanate grains [5].

The existence of the microstructures exhibiting two distinct zirconia morphologies was clearly visible during TEM studies. Fig. 6a illustrates the zirconia particles concentrated at the grain boundaries whereas Fig. 6b shows the rounded morphology of the particles embedded within the grains. Both forms of zirconia also exhibited extensive twinning of the particles.

The occurrence of such twinning suggested the transformation of tetragonal phase to monoclinic zirconia. Such a transformation would not generally be expected in a zirconia stabilized with 3 mol % Y_2O_3 without the influence of some form of nucleation effect such as stress. However, it is probable that the size of

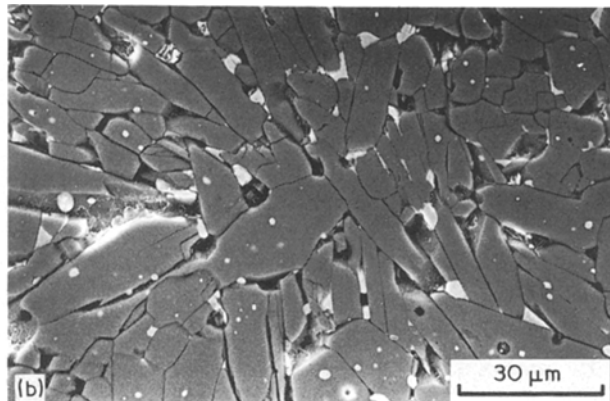


Figure 4 (a) Scanning electron micrograph of a polished section of a fully reacted sample sintered for 2 h at 1500 °C with a heating rate of 10 °C min⁻¹. (b) Scanning electron micrograph of a polished section of a sample containing 8 wt % ZrO_2 sintered at 1600 °C for 2 h.

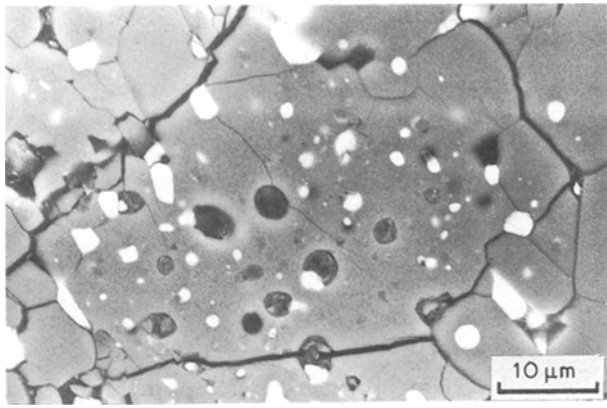


Figure 5 SEM of the polished surface of an aluminium titanate containing 8 wt % Y_2O_3 -stabilized ZrO_2 . The micrograph shows fine particles within matrix grains and cracking generated by the transformation of ZrO_2 particles.

the zirconia particles exceeds the critical value which can sustain the stabilization of the tetragonal phase; usually this is of the order of 1 to 2 μm [6]. The limited constraint offered by the aluminium titanate matrix, due to its low elastic modulus, would have the effect of further reducing the critical grain size for spontaneous transformation.

This dependence of the stability of the tetragonal phase on the particle size of the zirconia was also reflected in the XRD measurements, with change in firing temperature, Fig. 2. With the temperature as low as 1360 °C there was an appreciable amount of tetragonal phase. However, as the firing temperature was increased, the amount of monoclinic phase also increased at the expense of the tetragonal phase. This was consistent with the growth of the zirconia particles as the firing temperature was raised to 1600 °C.

As previously stated, the addition of zirconia to aluminium titanate resulted in an improved mechanical strength, despite the grain-boundary cracks obvious in Fig. 4b. This could be explained in terms of the zirconia particles being situated at the crack intersections, thus impeding the progress of an advancing crack. Alternatively there may also be a crack-branching mechanism operative, due to the additional microcracks generated by the transformation of the zirconia. Furthermore, the inhomogeneous nature of the elongated grains of the primary phase may also induce an increase in strength by an improved "keying" of the randomly oriented grains. It is probable that a combination of all these mechanisms contributes to the increased mechanical strength, even though the magnitude of the increase was relatively small.

The existence of additional microcracks due to the presence of zirconia can be observed in Fig. 5. It can be seen that cracks are emanating from the arrowed particles. The presence of strain lines was also noted around the transformed particles, Fig. 6. Further evidence was obtained on closer examination of the cooling data of the dilatometer curves. Fig. 7 shows that the material containing zirconia demonstrates an additional degree of expansion during cooling which

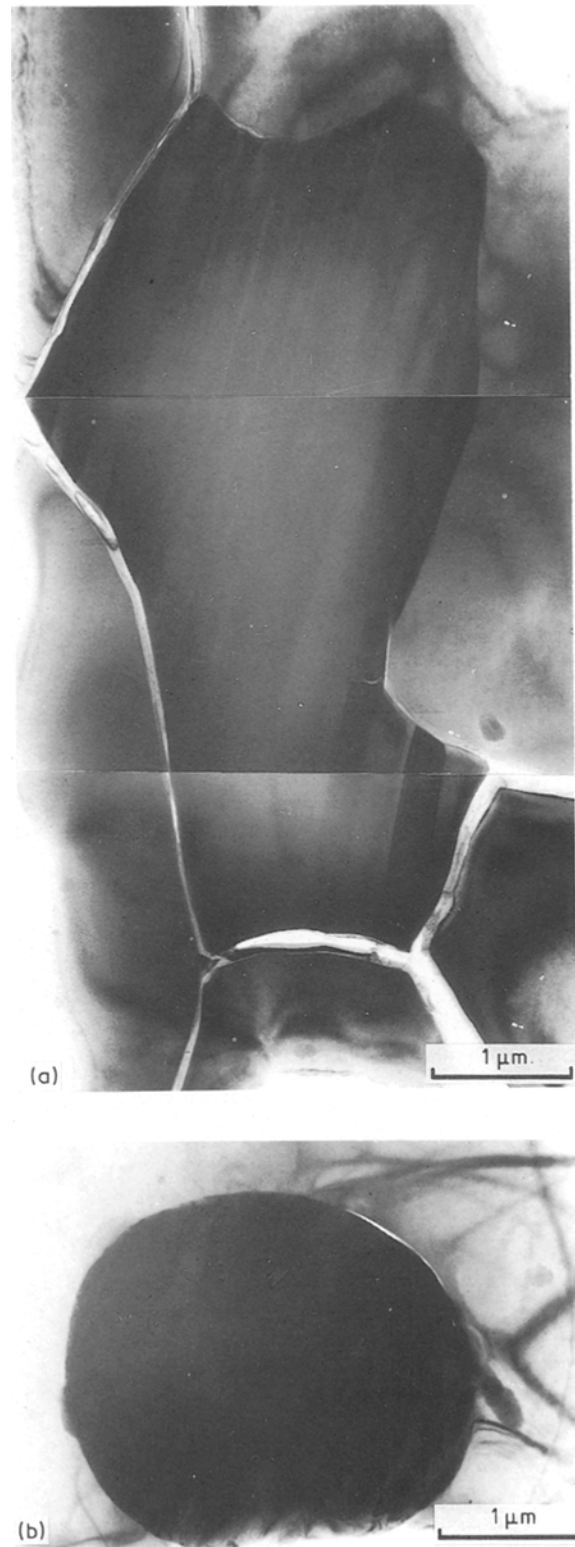


Figure 6 (a) Transmission electron micrographs of (a) a ZrO_2 particle at a grain boundary showing twinning and extensive cracking; (b) a ZrO_2 particle within grains showing rounded morphology and twinning. Twinning appears to have generated strain in the matrix.

is consistent with the microcracks observed in the microstructure generated on transformation of tetragonal zirconia to the monoclinic form. The presence of these microcracks became significant when examining the thermal expansion curves, shown in Fig. 8. The curves shown illustrate that the material doped with 5 wt % zirconia exhibits a zero thermal expansion coefficient up to 1300 °C. On the other hand, the pure

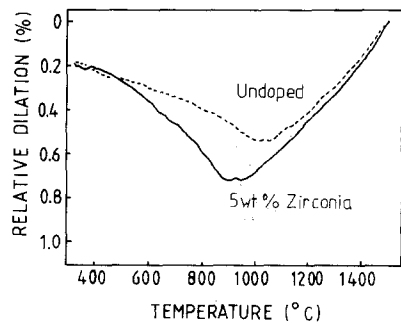


Figure 7 Effect of zirconia on the microcrack initiation temperature.

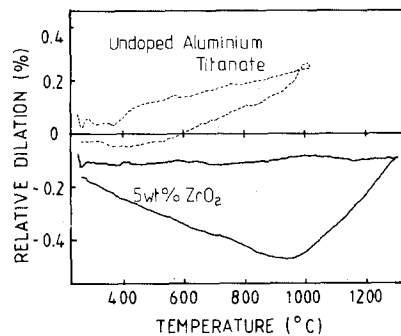


Figure 8 The effect of zirconia on the thermal expansion of aluminium titanate.

aluminium titanate has a coefficient of $2.9 \times 10^{-6} \text{ K}^{-1}$ up to 1000°C . Such behaviour can thus be explained in terms of the additional microcracks generated in the zirconia-doped material.

4. Conclusions

1. The addition of zirconia to an ultrafine mixture of alumina and titania resulted in an improved sintered density and increased mechanical strength of the sintered product.

2. The improved strength was attributed to a combination of better "keying" of the randomly oriented elongated grains and the operation of crack deflection and branching mechanisms.

3. The latter mechanism was made possible by the presence of additional microcracks generated by the transformation of the zirconia particles.

4. The presence of extra microcracks resulted in a zero thermal expansion coefficient up to 1300°C for the zirconia-doped material.

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